

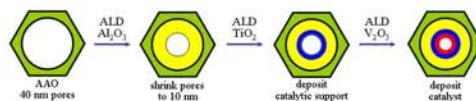
# New Directions in Catalysis: Nanostructured Membranes

M. Pellin (MSD), P. Stair (NWU, CHM), L. Curtiss (MSD), J. Elam (ES), H. Feng (CHM), H. Wang (MSD), L. Iton (MSD), P. Zapol (MSD), J. Schluter (MSD), P. Redfern (CHM), S. Zygmunt (Valparaiso), H. Kung (NWU)

## Introduction

- This poster presents an overview of new directions in catalysis based on the nanoporous membranes developed in the Materials Science Program.
- The project is a multidisciplinary one involving ANL (Materials Science and Chemistry Divisions) and Northwestern University
- Advance molecular-level understanding and control of pathways for selective catalytic oxidation by exploiting a new and unique architecture for ultra-uniform catalysts.
- Four synergistic components: synthesis, characterization, catalytic activity, and theory

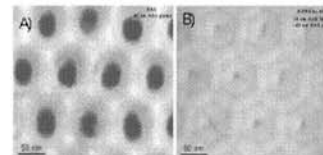
## Catalytic Nanoporous Membranes



Synthesis based on anodized aluminum oxide (AAO) and atomic layer deposition (ALD)

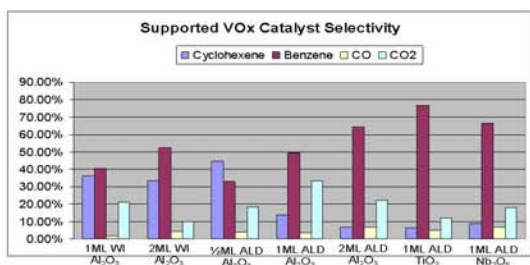
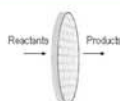


ALD Viscous Flow Reactor



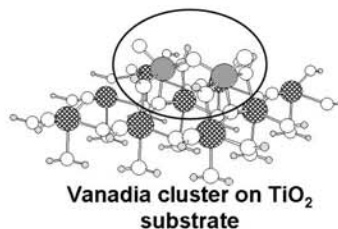
Plan view SEM image of (A) 40 nm AAO material and (B) 40 nm AAO material coated with 15 nm of alumina.

## Conversion and Selectivity for catalytic oxidation dehydrogenation (ODH) of cyclohexane

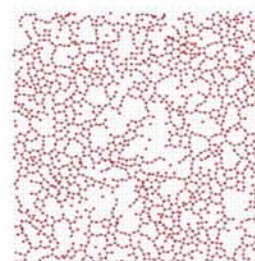


Cyclohexane ODH selectivity measured on various supported vanadia catalyst on various ALD/AAO membranes. (WI denotes wet impregnation.) The results show that selectivity in the membranes can be controlled by the ALD process.

## Simulation And Modeling: Materials and Reactions



Density functional results indicate a large barrier decrease for reduced vanadia clusters on a  $\text{TiO}_2$  substrate



A snapshot of the top 3 Å of the amorphous alumina surface structure (top view)

## Accomplishments

We have demonstrated a facile synthesis method for catalytic membranes. The method allows control of both pore wall diameter and composition with atomic level precision. Membranes of AAO coated with ALD alumina exhibit high specific vanadia conversions and control of specificity for the ODH of cyclohexane to cyclohexene. Computational studies show that the substrate can have a large effect on dehydrogenation barriers.

## Future

- Exploit the new type of nanoporous material described above to develop a predictive understanding of chemical reactivity that will lead to unprecedented atomic level control of catalysis
- Create materials that can function as supports for encapsulated catalytic clusters, complexes, or nanoparticles and then systematically investigate prototypical selective oxidation reactions to gain a molecular level understanding how to control catalytic reactions
- The catalytic reactions will be extended beyond cyclohexane to  $\text{C}_2$ ,  $\text{C}_3$ , and  $\text{C}_4$  hydrocarbons that are of great interest to the chemical industry as well as other reactions.

Pellin, M. J. et al. *Catalysis Letters* 102, 127-130 (2005).